Journal of Power Sources 219 (2012) 325–332

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Performance of an active direct methanol fuel cell fed with neat methanol

Nobuyoshi Nakagawa*, Takuya Tsujiguchi, Syu Sakurai, Ryota Aoki

Department of Chemical and Environmental Engineering, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

HIGHLIGHTS

- An active DMFC fed with a neat methanol was firstly fabricated and successfully operated.
- The neat methanol use was enabled by the electrode structure with a porous carbon plate.
- A similar performance compared with that of the conventional DMFC with a very low air-flow rate.
- It showed 62 mW cm^{-2} power density and 0.28 overall efficiency at 65 °C.

ARTICLE INFO

Article history:
Received 30 May 2012
Received in revised form
16 July 2012
Accepted 21 July 2012
Available online 31 July 2012

Keywords:
Active direct methanol fuel cell
Novel electrode structure
Air-flow rate
Methanol crossover
Overall power generation efficiency

ABSTRACT

Based on our previous fundamental studies on the mass transport and electrode performance of a passive direct methanol fuel cell (DMFC) with a novel electrode structure using a porous carbon plate (PCP), a single cell of an active DMFC with this structure and having the extended active area of 30 cm^2 was designed and fabricated. The power generation characteristics of the active DMFC using neat methanol (99.8 wt%), including the power density, the rate of methanol crossover and the overall energy conversion efficiency of the single cell, were investigated at different operating conditions. The highest power density was obtained with 100% methanol in the different methanol concentration range of 70–100 wt% suggesting that the electrode structure with PCP was set for the 100% methanol use under the active conditions. The maximum power density of 62 mW cm^{-2} with an overall efficiency of 0.28 was obtained at 65 °C. The performance was comparable or relatively higher than those of the other DMFCs using diluted methanol solutions ranging from 3 to 10 wt%. The performance was established in humid air around saturation at the small feed rate less than one-fourth that used for the DMFCs with the diluted methanol solutions. The single cell was continuously operated for 100 h with an almost constant power density.

1. Introduction

For the efficient utilization of fossil fuels and suppression of the emission of greenhouse gases, research and development around the world has focused on fuel cells as a promising technology with a high energy conversion efficiency and low emissions. Direct methanol fuel cells (DMFCs) have received much attention as a new power source for ubiquitous electric devices, portable power devices and transportation because of their high theoretical energy densities and easy use of the liquid fuel. However, there are still problems with the DMFC involving methanol crossover and sluggish electrode reactions as well as catalyst durability.

Due to methanol crossover, the open circuit cell voltage of the DMFC is as low as nearly half the theoretical value, and then the overall energy conversion efficiency is lower than that of polymer electrolyte fuel cells using hydrogen. The rate of methanol crossover increased with the increase in the methanol concentration, therefore, the concentration of methanol used in the conventional DMFC is usually limited in the range of 3–10 wt%. A DMFC system operated with such a low methanol concentration requires a large storage tank for the diluted methanol solution, and/or a complex system for recycling water from the cathode, therefore, the energy density of the DMFC system is not expected to be high.

We have proposed a unique electrode structure that makes the direct use of neat methanol (almost 100% methanol) in a DMFC possible using a porous carbon plate (PCP) at the anode [1–6]. The electrode structure increased the energy density of a passive DMFC by a factor of 20 [5] by reducing the methanol crossover and reducing the flooding at the cathode. Through several investigations regarding the relationship between the cell performance and

* Corresponding author. Tel.: +81 277 30 1458; fax: +81 277 30 1457.
E-mail addresses: nakagawa@cee.gunma-u.ac.jp, nobnaka@sannet.ne.jp (N. Nakagawa).

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2012.07.062

the mass transport in a passive DMFC with PCP, it has been clarified that a thin gas layer is formed between the anode and the methanol solution in the electrode structure with PCP, then the methanol would be supplied as a vapor to the anode. Hence, the DMFC using PCP is considered as a vapor-fed DMFC in principal, although a liquid methanol solution is used. The mass transport of the methanol was obstructed by both the PCP and the gas layer resulting in the reduced rates of methanol crossover, below 1/10 that without PCP [2], depending on the pore structure, thickness of the PCP and that of the gas layer [2]. The vapor feed induced the water back-diffusion from the cathode to the anode through the membrane [2,5,7], and this made flooding unlikely to occur at the cathode [3]. Under such conditions, the humidification of air at the cathode is important to hydrate the membrane and increase the power density [7,8]. The electrode structure with PCP was applied to the anode of a 2 W passive stack and the power generation using neat methanol was successfully demonstrated [4]. Similar to the DMFC with PCP, some other types of vapor feed DMFCs, that can use high methanol concentration solutions have been reported as a passive or a semi-passive system [7,9,10]. However, there has not yet been an active DMFC operated with neat methanol. In the passive or semi-passive systems, the operating conditions including temperature, flow rate of fuel and that of air as well as the air humidity are not consciously controlled, thus the power density of the passive DMFC was not very high. For a power generation system, an active system with control of the operating conditions is preferred for achieving a high power density and high energy conversion efficiency.

In a liquid feed DMFC system, flooding usually easily occurs so that a high volume of air, about twenty times the stoichiometry, is sometimes fed to the cathode in order to remove the liquid water droplets and to avoid cathode flooding, resulting in consuming almost one-third the electric power generated by the DMFC for the blower to feed the required air [11]. An alternative active DMFC system using PCP is expected to provide a more efficient power generation system with reduced parasitic load for the air feed and liquid fuel supply, because, as mentioned above, the flow rate of the air to the cathode and that of the liquid methanol to the anode can be reduced in the system with PCP and the utilization of a high methanol concentration, respectively. However, there was no report of an active type DMFC operated with neat methanol and its power generation performance.

In this study, an active DMFC using PCP, with a 30-cm^2 active electrode area, was fabricated based on our previous studies of the passive systems, and the power generation performance of the active DMFC was investigated by feeding neat liquid methanol. The cell structure using PCP was introduced and the effect of the operating conditions, i.e., anode discharging gas pressure, methanol concentration, air-flow rate, air humidity, and temperature, on the power generation characteristics including the power density, methanol crossover, and the overall power generation efficiency was investigated. The result was discussed by focusing on the difference in the mass transport mechanism from the conventional liquid feed DMFC systems.

2. Experimental

2.1. DMFC structure with a porous carbon plate

Fig. 1 shows a schematic illustration of the single cell structure with the PCP, (a), and the experimental setup of the DMFC power generation, (b), used in this study. The cell was designed and fabricated in a cooperative study with Chemix Co., Ltd., Japan. The cell consisted of an air plate, an MEA, a gas spacer, a porous carbon plate (PCP) and a fuel plate. The active area of the MEA was 30 cm^2

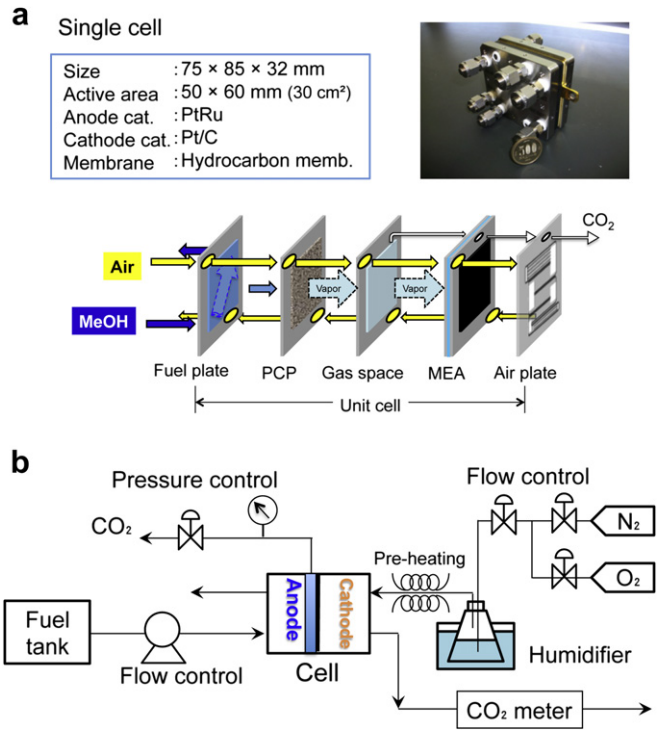

Fig. 1. Schematic diagram of the active DMFC with PCP (a) and the experimental setup (b) used in this study.

and was 6 times larger than that used in our previous test cells [2,3,5]. In contrast to the common cell structure, the PCP and the gas spacer were used between the anode of the MEA and the fuel plate. All of the plates and the gas spacer were made of carbon. The air plate had flow channels of 2.0 mm width and 0.8 mm depth, and the fuel plate had a methanol flow-field. The single cell was designed as a stack unit. The thickness of the PCP and the spacer was 0.5 and 1.5 mm, respectively, and then the total thickness of the unit, including the fuel plate and the air plate, was 6 mm. The PCP had small pores with the average size of a few micrometers. In this cell structure, when the power generation started by feeding a methanol solution to the methanol flow-field, the CO_2 gas produced at the anode accumulated in the gas space and formed a gas layer between the anode and the PCP [1,2,12,13]. Some of the gas in the gas layer can be discharged through a hole and a back-pressure valve as shown in the figure. This electrode structure significantly reduces the methanol crossover and allows a direct feeding of 100% liquid methanol [1,3,5].

For the MEA, a hydrocarbon membrane, of which the proton conductivity and methanol permeability were comparable to those of Nafion-115 [14,15], was used as the electrolyte, and PtRu black (5 mg$_{-PtRu}$/cm^2) and Pt/C (3 mg$_{-Pt}$/cm^2) were used as the catalyst for the anode and cathode, respectively.

The methanol in the reservoir was supplied to the cell by a pump through a 4-mm i.d. stainless tube. The DMFC was operated by feeding the liquid methanol solution and the humidified air at atmospheric pressure to the anode and the cathode, respectively. The temperature of the cell was controlled using rod heaters inserted into the end plates, made of stainless steel, and running cooling water through them, although they are not shown in the figure. The methanol used in this study was of chemical grade, 99.8 wt%, purchased from Wako Pure Chemical Industries, and the water used for diluting the methanol, in some cases, was distilled water (Kyoei Pharmaceutical Co., Ltd.), A4 grade of JIS K0557 [16].

2.2. Measurement of the DMFC performance

The experiment was started by varying the discharging gas pressure to obtain the higher performance. The discharging gas pressure is a unique parameter for this type of DMFC [13]. It affects the mass transport of the methanol through the PCP [13] and that of the water by the hydraulic pressure difference between the membrane surfaces as well as the evaporative loss of the methanol. Since this is the first time to operate an active DMFC with PCP, the effect of the discharging gas on the performance was investigated in order to find the optimum pressure. The effect of the methanol concentration was then investigated between 70 and 100 wt% to check the optimum methanol concentration for the designed electrode structure. With the discharging gas pressure optimized and using the neat methanol, the current–voltage relationship and the rate of methanol crossover were measured at different operating conditions, including the methanol feed rate, air feed rate, air humidity and temperature.

The electrochemical measurements were conducted using an electric load (PLZ-4W, Kikusui Co., Ltd.). The ohmic resistance of the cell was measured using a digital AC impedance meter (FC-100R, CHINO Co., Ltd.). The rate of methanol crossover (MCO) was calculated from the CO_2 concentration in the effluent gas from the cathode outlet measured by an IR CO_2 meter (CGT-7000, Shimadzu Co., Ltd.).

2.3. Evaluation of the overall power generation efficiency

Based on the cell performance including the methanol crossover, the overall power generation efficiency of the DMFC was calculated as follows.

$$\text{Efficiency} = \left(\frac{\Delta G^\circ}{\Delta H^\circ}\right)\left(\frac{V_{\text{cell}}}{V_{\text{Theoretical}}}\right)\left(\frac{i_{\text{cell}}}{i_{\text{cell}} + i_{\text{crossover}}}\right) \quad (1)$$

where ΔG° is the standard Gibbs free-energy change for the methanol oxidation reaction:

$$CH_3OH_{(L)} + (3/2)O_2 \rightarrow CO_2 + 2H_2O_{(L)} \quad (2)$$

and ΔH° is the standard enthalpy change of the reaction, V is the cell voltage and i is the current density of the fuel cell. The crossover current density, $i_{\text{crossover}}$, was calculated from the rate of the measured methanol crossover.

3. Results and discussion

3.1. Effect of the discharging gas pressure and the methanol concentration

During the operation of the DMFC, the pressure of the discharging gas from the anode gas space is one of the operational parameters. It has been reported that the pressure influences the mass transport of methanol and water in the cell, and hence, the rate of the electrode reaction at the anode, and the power generation performance of the passive DMFC with PCP [13]. The effect of the discharging gas pressure was then investigated. Fig. 2 shows the effect of the discharging gas pressure from the anode gas space on the power generation characteristics, the cell voltage and the power density vs. the current density, Fig. 2a, and the rate of methanol crossover and the overall power generation efficiency vs. the current density, Fig. 2b, were measured at the neat methanol and the humidified air (RH 100%) at feed rates of 2 mL min^{-1} and 0.3 L min^{-1}, respectively, at 45 °C. The pressure slightly affected the current–voltage (i–V) and the current–power density (i–P) performance as shown in Fig. 2a. Although a relatively high power density, 40 mW cm^{-2}, was obtained at the middle pressure, 15 kPa (gauge pressure), the direct effect of the pressure on the electrode reaction kinetics would be low due to the small measured pressure change from 10 kPa to 30 kPa. On the other hand, the rate of methanol crossover (MCO) decreased with the increasing pressure as shown in Fig. 2b, in accordance with that observed for the previous passive DMFC with PCP [13]. The high pressure would increase the distance for diffusion of the methanol vapor in the pores of the PCP by changing the position of the gas/water interface in the PCP. Since the best power density and the best efficiency were obtained at a 15 kPa pressure, the pressure was set at 15 kPa in this experiment.

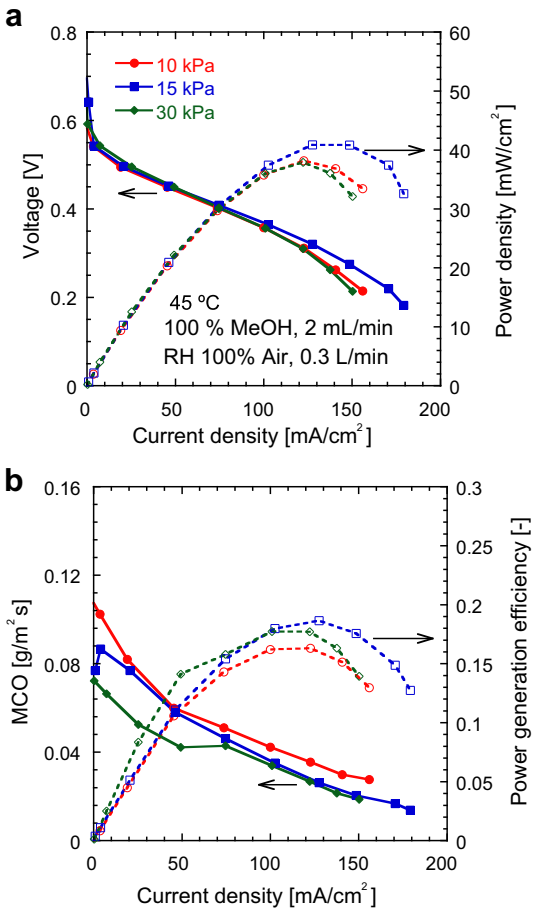

Fig. 2. Performance of the active DMFC with PCP obtained for the different discharging gas pressures, 10, 15 and 30 kPa, at 100% methanol (2 mL min^{-1}), air (RH 100%, 0.3 L min^{-1}), 45 °C. Relationship between the current density and the cell voltage as well the power density, (a), and MCO with the overall power generation efficiency, (b).

Fig. 3 shows the power generation characteristics, i.e., i–V curve, power density, MCO and the power generation efficiency, for the DMFC with PCP at different methanol concentrations ranging from 70–100 wt% (99.8 wt%) at 45 °C. With the increasing methanol concentration, the i–V performance was especially improved in the region of high current densities. At low methanol concentrations, from 70–90 wt%, the limiting current appeared and it increased with the increasing concentration. The best power density of 40 mW cm^{-2} was then obtained at 100%. In the DMFC with PCP, the optimum methanol concentration for the power density can be controlled by factors affecting the resistance of the methanol transport through the PCP and the gas layer, i.e., porosity and thickness of the PCP and the gas layer [5]. The results shown in

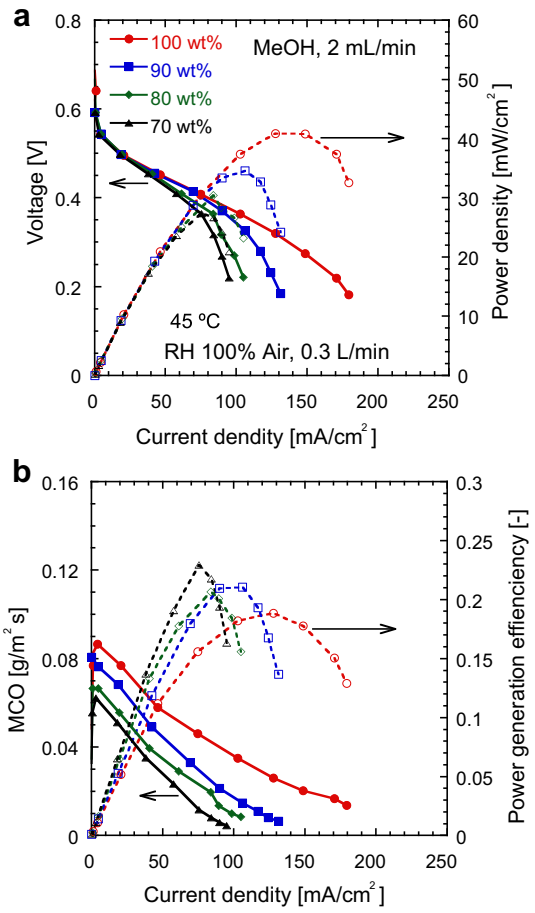

Fig. 3. Performance of the active DMFC with PCP obtained for the different methanol concentrations in the range from 70 to 100 wt% at 2 mL min^{-1}, air (RH 100%, 0.3 L min^{-1}), 45 °C. Relationship between the current density and the cell voltage as well the power density, (a), and MCO with the overall power generation efficiency, (b).

Figs. 2 and 3 clarified that these factors in the electrode structure were successfully adjusted for 100% methanol use under the active operating conditions. On the other hand, in Fig. 3b, the MCO clearly increased with an increasing concentration. MCO causes an energy loss in the power generation as shown in Eq. (1), and the power generation efficiency decreased with the increase in the methanol concentration. The relationship in Fig. 3a showed a common line, but that in Fig. 3b showed different lines for the different methanol concentrations at the low current densities below 50 mA cm^{-2} suggesting the weak relationship between the power density and the energy efficiency in the active DMFC. Different from the case of a passive DMFC using air, the relationship between the *i–V* or *i–P* performance and the MCO or the efficiency was not strongly related to each other. This would be due to the relatively high air-flow rate, 0.3 L min^{-1}, that corresponds to 5 times the stoichiometry at 100 mA cm^{-2}, compared to the air-flow in the passive DMFC, that eliminates the effect of crossover methanol at the cathode, although the air-flow rate with 5 times the stoichiometry was much lower than that used for the conventional liquid feed DMFCs with dilute methanol solutions as will be discussed later. The common *i–V* relationship at the low current densities in Fig. 3a meant that the performance was not affected by the cathode conditions and was governed by the reaction at the anode. And the *i–V* curves at the high current densities, over 50 mA cm^{-2}, were controlled by the methanol transport to the anode. Hereafter, only the performance with the neat methanol will be discussed.

3.2. Effect of the methanol flow rate, the air-flow rate and the air humidity

Fig. 4 shows the effect of the methanol flow rate on the power generation performance at 45 °C. The methanol flow rate slightly affected the performance. This would be related to the transfer of methanol through the PCP and the gas layer, therefore, the change in the methanol flow rate had a slight effect on the mass transfer rate. Based on three different flow rates, the best power density was obtained at the lowest flow rate, 2 mL min^{-1}, as shown in Fig. 4a, and the best efficiency was also obtained at the lowest flow rate showing the lowest MCO as shown in Fig. 4b. The lowest flow rate, 2 mL min^{-1}, corresponds to 27 times the stoichiometry at 100 mA cm^{-2}. It is still too high and may be further reduced for a better performance, although it could not be confirmed in the experiment because of the limitation in controlling the flow rate. The low flow rate during operation is beneficial for the DMFC system to reduce the auxiliary power for the fuel supply and then increase the system efficiency.

Fig. 5 shows the effect of the air-flow rate on the performance at 45 °C. The increase in the flow rate, up to 0.4 L min^{-1}, increased the cell voltage at the low current densities, as well as increasing the maximum current density, and hence the power density increased with the increasing air-flow rate. The maximum power densities at 0.2 L min^{-1} and 0.8 L min^{-1} were 35 mW cm^{-2} and 56 mW cm^{-2}, respectively. The air-flow rate of 0.2 L min^{-1}, that corresponds to 3.5

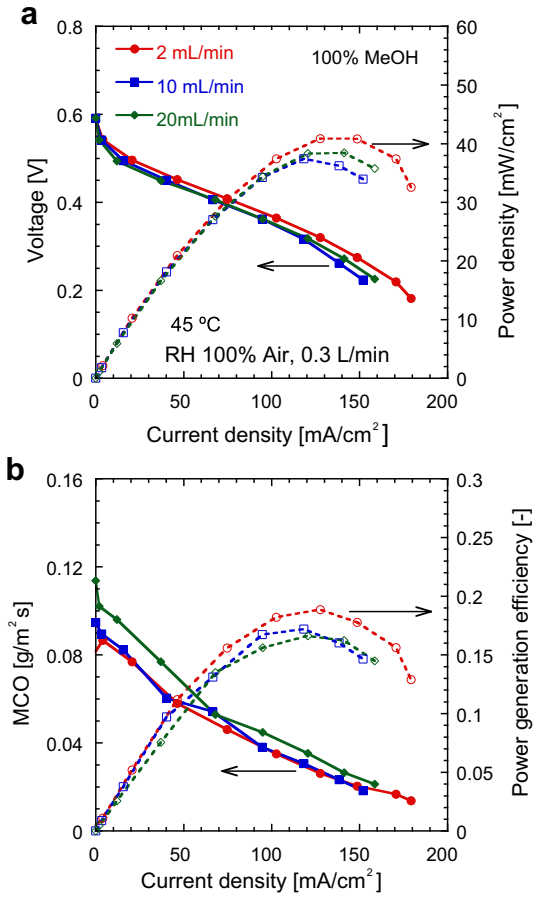

Fig. 4. Effect of the methanol flow rates on the active DMFC performance with air (RH 100%, 0.3 L min^{-1}) at 45 °C. The methanol solution was the 100% methanol. Relationship between the current density and the cell voltage as well the power density, (a), and MCO with the overall power generation efficiency, (b).

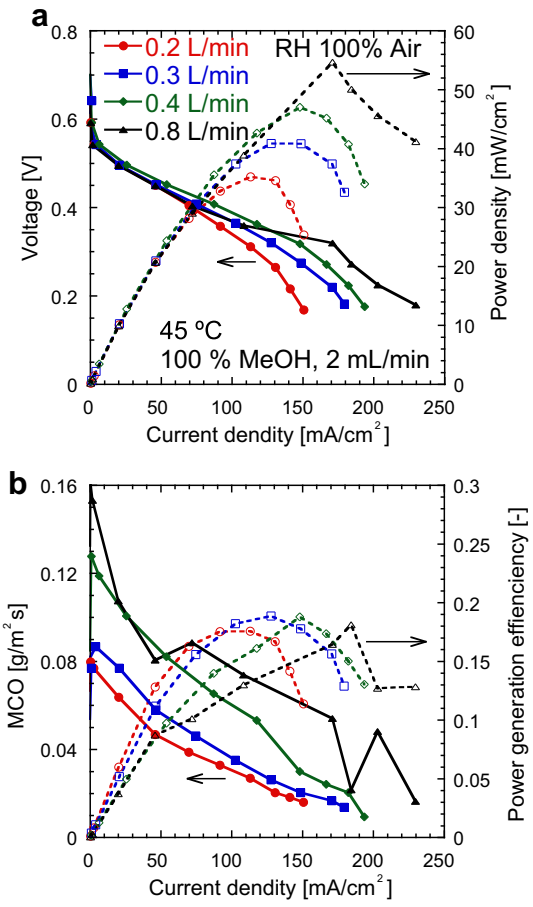

Fig. 5. Effect of the air-flow rates on the active DMFC performance with the 100% methanol (2 L min^{-1}) at 45 °C. Relative humidity of the air was 100%. Relationship between the current density and the cell voltage as well the power density, (a), and MCO with the overall power generation efficiency, (b).

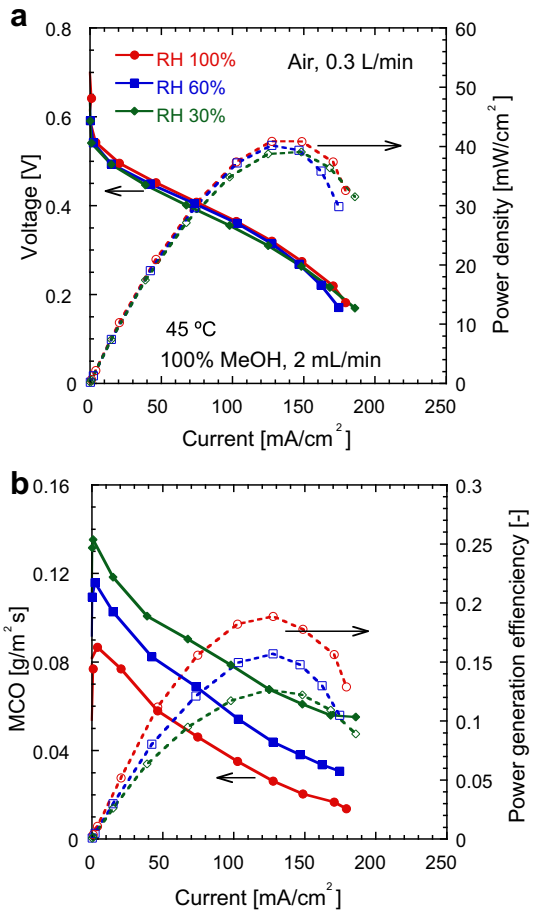

Fig. 6. Effect of the air humidity on the active DMFC performance with the 100% methanol (2 L min^{-1}) at 45 °C. The air-flow rate was 0.3 L min^{-1}. Relationship between the current density and the cell voltage as well the power density, (a), and MCO with the overall power generation efficiency, (b).

times the stoichiometry at 100 mA cm^{-2}, was not enough to reduce the cathodic overvoltage to a negligibly low value at the high current densities, and then the cell voltages at the high current densities increased with the increasing air-flow rate. However, the increase in the air-flow rate caused an increase in the MCO, in agreement with a previous report [17], as shown in Fig. 5b. The MCO at the open circuit condition of 0.8 L min^{-1} was 0.16 g/m^{2}s that was almost double that at 0.2 L min^{-1}. Although the difference in the MCO at the different air-flow rates was quite high, it did not affect the *i*–*V* and *i*–*P* curves at the low current densities below 50 mA cm^{-2} as shown in Fig. 5a similar to that at Fig. 3a. The effect of the crossover methanol at the cathode was eliminated by the relatively high air-flow rate that was more than 3 times greater than that of the stoichiometry at 100 mA cm^{-2}. Then the *i*–*V* curves at the low current densities were similar to each other. On the other hand, the *i*–*V* performance would be controlled by the oxygen supply to the cathode in the high current density region over 50 mA cm^{-2} where the oxygen supplying rate was increased with the increase of the air-flow rate.

Fig. 6 shows the effect of the air humidity on the performance at 45 °C. As shown in Fig. 6a, the air humidity slightly affected the *i*–*V* curve and the power density in the humidity range from 30% to 100% at the temperature. However, the air humidity strongly affected the MCO and the power generation efficiency as shown in Fig. 6b. The MCO decreased with the increasing relative humidity, RH, and the MCO at the open circuit condition was 0.135 g m^{-2} s^{-1}, 0.115 g m^{-2} s^{-1} and 0.08 g m^{-2} s^{-1} at RH 30%, 60% and 100%, respectively. The maximum power generation efficiency was 0.12, 0.16 and 0.20 at RH 30%, 60% and 100%, respectively. According to the cases in Figs. 3 and 5, the MCO did not affect the *i*–*V* performance under the relatively high air-flow rate. The similar *i*–*V* curves for the different air humidity levels would be due to the similar conditions for the methanol supply to the anode and that for the oxygen supply to the cathode at the different air humidity levels. For the DMFC with PCP, it is known that the water transport from the cathode to the anode through the membrane occurs due to the diffusion mechanism [2]. The direction of the water diffusion is counter to that of the MCO. Hence, the higher humidity would cause a higher water diffusion rate, and hence, the smaller MCO.

In general, the MCO of DMFCs operating with a low concentration liquid methanol solution is slightly affected by the air humidity, because the membrane is highly hydrated with water at the anode. Hence, the strong effect of the air humidity on the MCO is characteristic to the DMFC with PCP [2] similar to that at the vapor feed DMFCs [7,8]. It is necessary for the efficient power generation in this type of DMFC to be operated with a very humid air, like at RH 100%, at this temperature. This is suitable for the DMFC because the water saturation in the air channel is easily achieved by the water production of the cathode reaction. Comparing to the liquid feed DMFC that is usually operated with a high air-flow rate, sometimes more than 20 times that of the stoichiometry [11], to avoid the cathode from flooding, the DMFC

with PCP can be operated at a lower air-flow rate while keeping the humidity high as well as avoiding flooding, because some of the water produced at the cathode is removed by diffusion to the anode. The lower air-flow rate reduces the auxiliary power requirement for the air-flow in the DMFC system and increases the system efficiency.

3.3. Effect of temperature

Fig. 7 shows the effect of the operating temperature on the performance of the DMFC. The temperature had a significant effect on the power density, and the higher the temperature, the higher the i–V performance and the higher power density. These were explained by the increased rates of the electrode reactions, both at the anode and the cathode, and the increased ionic conductivity of the electrolyte with the temperature increase. The different i–V curves at the different temperatures in the figure should be mainly due to the different overvoltage for the electrode reactions at the different temperatures, and would not be due to the MCO based on the previous results shown in Figs. 3, 5 and 6 where the i–V curve did not affected by the MCO. The maximum power generation efficiency increased with the temperature, and reached 62 mW cm^{-2} at 65 °C, that was more than double that at 30 °C. On the other hand, the MCO also increased with an increase in the temperature due to the increased methanol permeability with the increase in the temperature. The effect of the increase in the MCO was not related to the power density in the active DMFC as mentioned for the effect of other parameters shown in Figs. 3–6.

The boiling point of the neat methanol is about 65 °C and the effect of temperature in this figure was limited to 65 °C. The effect of temperatures higher than 65 °C will be reported in the future.

3.4. Long-term operation

Fig. 8 shows the power density profile of the DMFC with PCP at 0.3 V and 45 °C for 100 h. During the long-term operation, although the initial power density of about 40 mW cm^{-2} decreased to 30 mW cm^{-2} in 5 h, the power density remained almost constant for 100 h, but showing several noise spikes that would be caused by refilling of the methanol. This figure confirmed that the DMFC with PCP could be operated at the low air-flow rate for a long time. Since the noise spike showed an increased power density, the degradation may be related to limiting the supply of the methanol or oxygen to the electrodes. The reason for the initial degradation of the power density has not yet been clarified, and will be a future subject.

3.5. Comparison of the performance with that of liquid feed DMFCs

Table 1 summarizes the power generation performance at 60 °C for the different DMFC single cells in this study. Except for this study, the performances were obtained from the conventional liquid feed DMFCs [17,19–22]. The maximum power density was evaluated from their i–V curve at 60 °C, and the maximum efficiency was calculated from the i–V curve with their methanol crossover rate shown in their reports [17,19–22]. The maximum power density was ranged between 28 mW cm^{-2} and 80 mW cm^{-2}, and the maximum power generation efficiency was between 0.1 and 0.35 among the different DMFCs. Our DMFC with PCP using 100% methanol had values of 52 mW cm^{-2} and 0.27 [–] for the maximum power density and the maximum efficiency, respectively. The power generation performance of the DMFC with PCP was comparable or relatively higher in performance than that of the liquid feed DMFCs using the diluted methanol solutions. This would mean that the actual circumstances of the electrode surface, i.e., activity of methanol at the anode surface and that of oxygen at the cathode surface, were similar to each other, irrespective of the type of DMFC and the methanol concentration of the fuel, assuming that the catalytic activity of the electrode and the properties of the electrolyte were roughly similar to each other. The similar methanol activity at the anode of the DMFC with PCP to that of the liquid

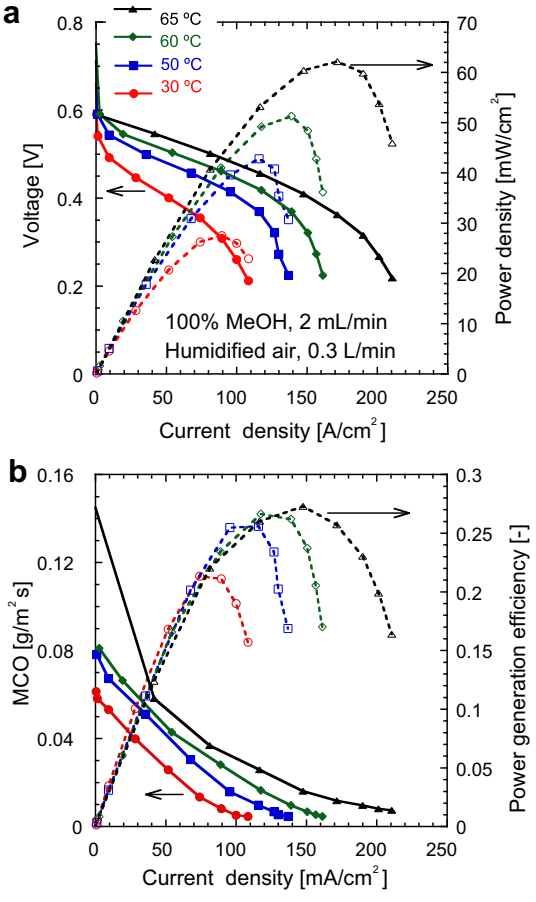

Fig. 7. Effect of temperature on the active DMFC performance with the 100% methanol (2 mL min^{-1}) and humidified air (0.3 L min^{-1}). Relationship between the current density and the cell voltage as well the power density, (a), and MCO with the overall power generation efficiency, (b).

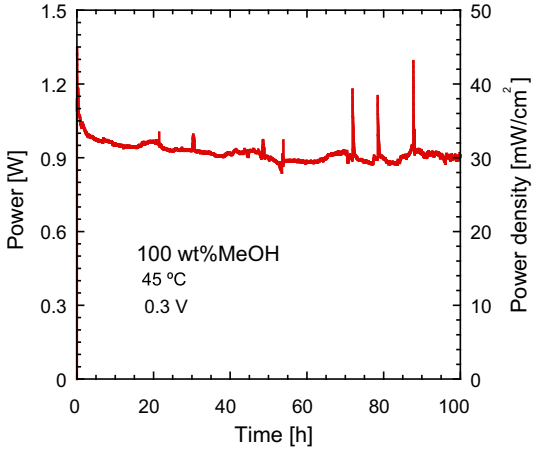

Fig. 8. Power and the power density with time during the constant voltage operation using the 100% methanol at 0.3 V, 45 °C for 100 h.

Table 1
Comparison of active DMFC single cell performance at 60 °C (and 65 °C) among different studies.

Year [Ref.]	Membrane anode catalyst cathode catalyst	Active area [cm^2]	Oxidant and its flow rate [ml/(min cm^2)]		Fuel (MeOH conc.) and its flow rate [ml/(min cm^2)]		Max. power density [mW/cm^2]	Max overall efficiency [−]	Note
2011 [23]	Nafion-117 PtRu 2 mg cm^{-2} Pt 1.3 mg cm^{-2}	22.1	Air	42	3.25 wt%	0.05	62 57 40	0.20 0.21 0.22	MEA GG MEA GM MEA MM
2010 [21]	Nafion-117 PtRu 4.0 mg cm^{-2} Pt black 4.0 mg cm^{-2}	5	Air humidified at 338 K	40	–	0.60	–	0.23	
2009 [24]	SPI PtRu/C (2.2 mg-PtRu/cm^2) Pt/C (1.67 mg-Pt/cm^2)	5	Humidified O_2 Humidified air	37 110	5 wt% 5 wt%	0.20 0.20	77 68	0.23 0.21	At 200 mA cm^{-2} At 200 mA cm^{-2}
	Nafion-112 PtRu/C (2.2 mg-PtRu/cm^2) Pt/C (1.67 mg-Pt/cm^2)	5	Humidified O_2 Humidified air	37 110	5 wt% 5 wt%	0.20 0.20	72 66	0.11 0.11	At 200 mA cm^{-2} At 200 mA cm^{-2}
2008 [17]	GEFC-117 PtRu 4 mg cm^{-2} Pt 4 mg cm^{-2}	12.25	Air	200	3.25 wt%	0.04	60	0.24	
2007 [22]	GEFC-117 PtRu 4 mg cm^{-2} Pt 4 mg cm^{-2}	20	Air	122	3.25 wt%	0.02	28	0.1	
2007 [20]	Nafion 117 PtRu 2 mg cm^{-2} Pt 2 mg cm^{-2}	5	Air Air O_2	120 120 40	1.63 wt% 3.25 wt% 3.25 wt%	0.05 0.05 0.05	60 73 73	0.28 0.24 0.24	
2004 [19]	PSSA-PVDA PtRu 8 mg cm^{-2} Pt 8 mg cm^{-2}	25	O_2	5	3.25 wt%	–	34	0.35	
This work	Hydrocarbon PtRu black 5 mg cm^{-2} Pt/C (3 mg-Pt/cm^2)	30	Humidified air	10	99.8 wt%	0.07	52 62	0.27 0.28	 At 65 °C

feed DMFC with a diluted methanol solution has already been confirmed in our previous study [18]. However, a similar power generation performance was obtained at the different operating conditions depending on the type of DMFC, i.e., DMFC with or without PCP and the liquid feed of the diluted methanol solution or the vapor feed with the neat methanol. It should be noted that the specific air-flow rate, i.e., the volume flow rate of air divided by the active electrode area, of the DMFC in this study, was the lowest among the DMFCs in the table, except for the case with the PSSA-PVDA membrane [19] that showed a very low methanol permeability. It was one-fourth, one-tenth or less compared to the other DMFCs. This is because the flooding does not easily occur at the cathode for this type of DMFC due to the different mass transport situation in the cell as already mentioned. Generally, the high flow rate of air, more than twenty times the stoichiometry, is used for the liquid feed DMFC [11] to remove the liquid water droplets from the cathode and to avoid the cathode from flooding. Such a high air-flow rate operation consumes a relatively high amount of electricity generated by the DMFC, resulting in a reduced power output and power generation efficiency of the DMFC system. The low air-flow rate of the DMFC with PCP is quite attractive for reducing the auxiliary power for the air blowers in the system.

The above results showed a clear feature of the active DMFC with PCP, that has a comparable power density and efficiency with a very low flow rate of humid air. This feature increases the energy output and the energy conversion efficiency of the DMFC system by reducing the auxiliary power needed for the air blowers. The reduced volume of the fuel tank for the high concentration methanol would also be another advantage of the system in order to increase the volumetric energy density of the DMFC. On the other hand, the loss of the evaporated methanol with the discharge gas has to be taken into account for the system efficiency. With the increasing concentration of methanol and the operating temperature, the loss increases. The loss can be reduced by a proper method, e.g., cooling the discharging gas, increasing discharging gas pressure and recycling the condensed methanol. In this paper, we demonstrated an active DMFC using 100% methanol, the electrode structure with PCP can be setup for any optimum methanol concentration by adjusting the pore structure and the thickness of the PCP and the gas spacer. Actually, the appropriate concentration of methanol for the best performance of a system should be determined by a calculation for a given condition.

4. Conclusion

A single cell of the DMFC with the novel electrode structure using PCP having a 30 cm^2 active area was fabricated and operated under different conditions. The electrode structure was successfully setup for 100% methanol use and the power density of 42 mW cm^{-2} was obtained with neat methanol at 45 °C. The power generation performance with the power density of 52 mW cm^{-2} and the overall power generation efficiency of 0.27 at 60 °C was comparable or relatively higher than those of the previous liquid feed DMFCs at the same temperature. Such a similar performance was obtained at a very low air-flow rate, about one-fourth, one-tenth or less compared to that for the liquid feed DMFCs. At the same time, it was important for the feed air to be humidified at the saturation level to decrease the MCO and increase the overall efficiency. The DMFC with PCP was operated for 100 h at a constant power density.

Acknowledgment

The authors gratefully acknowledge the financial support given for a part of this study by The Iwatani Naoji Foundation.

References

[1] N. Nakagawa, M.A. Abdelkareem, K. Sekimoto, J. Power Sources 160 (2006) 105–115.
[2] M.A. Abdelkareem, N. Nakagawa, J. Power Sources 162 (2006) 114–123.
[3] M.A. Abdelkareem, N. Nakagawa, J. Power Sources 165 (2006) 685–691.
[4] T. Tsujiguchi, M.A. Abdelkareem, T. Kudo, N. Nakagawa, T. Shimizu, M. Matsuda, J. Power Sources 195 (2010) 5975–5979.

[5] M.A. Abdelkareem, N. Morohashi, N. Nakagawa, J. Power Sources 172 (2007) 659–665.
[6] M.A. Abdelkareem, T. Yoshitoshi, T. Tsujiguchi, N. Nakagawa, J. Power Sources 185 (2010) 1821–1828.
[7] X. Li, A. Faghri, C. Xu, Int. J. Hydrogen Energy 35 (2010) 8690–8698.
[8] M.S. Masdar, T. Tsujiguchi, N. Nakagawa, J. Power Sources 195 (2010) 8028–8035.
[9] S. Eccarius, F. Krause, K. Beard, C. Agert, J. Power Sources 182 (2008) 565–579.
[10] C. Xu, A. Faghri, X. Li, J. Electrochem. Soc. 157 (2010) B1109.
[11] T. Hatanaka, R&D Rev. Toyota CRDL 37 (2001) 59–64 (in Japan).
[12] N. Nakagawa, K. Kamata, A. Nakazawa, M.A. Abdelkareem, K. Sekimoto, Electrochemistry 74 (2006) 221–225.
[13] N. Nakagawa, M.A. Abdelkareem, J. Chem. Eng. Jpn. 40 (2007) 1199–1204.
[14] C.W. Lin, R. Thangamuthu, C.J. Yang, J. Membr. Sci. 253 (2005) 23–31.
[15] C.W. Lin, K.C. Fan, R. Tangamuthu, J. Membr. Sci. 278 (2006) 437–446.
[16] JIS K0557, Water Used for Industrial Water and Wastewater Analysis, 1998.
[17] A. Casalegno, R. Marchesi, J. Power Sources 185 (2008) 318–330.
[18] M.S. Masdar, T. Tsujiguchi, N. Nakagawa, J. Power Sources 194 (2009) 610–617.
[19] G.K. Surya Parkash, M.C. Smart, Q.-J. Wang, A. Atti, V. Pleynet, B. Yang, K. McGrath, G.A. Olah, S.R. Narayanan, W. Chun, T. Valdez, S. Surampudi, J. Fluorine Chem. 125 (2004) 1217–1230.
[20] R. Jian, Power and energy efficiency analysis of direct methanol fuel cell from single cell, in: L.O. Vasquez (Ed.), Fuel Cell Stack to DMFC System, Fuel Cell Research Trends, Nova Science Publishers, Inc, 2007. ISBN-13: 978-1-60692-750-2.
[21] S.H. Seo, C.S. Lee, Appl. Energy 87 (2010) 2597–2604.
[22] A. Casalegno, P. Grassini, R. Marchesi, Appl. Thermal Eng. 27 (2007) 748–754.
[23] A. Casalegno, C. Santoro, F. Rinaldi, R. Marchesi, J. Power Sources 196 (2011) 2669–2675.
[24] Z. Hu, T. Ogou, M. Yoshino, O. Yamada, H. Kita, K. Okamoto, J. Power Sources 194 (2009) 674–682.